Modeling & Simulation of Water Gas Shift Reaction

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ABSTRACT

The water-gas shift reaction, $CO + H_2O \leftrightarrow CO_2 + H_2$, provides a method for extracting the energy from the toxic CO by converting it into usable H_2 along with CO_2. For such an reaction depends on activity of catalyst so study of different metal based catalyst including Cu, Fe, Ni, Pd, Rh and Ru is in centre of interest. Generally all gas phase reaction is carried out in catalytic bed and all the reaction kinetics is based on some mechanism and also depends on catalyst property. Some of mechanism and kinetics of catalytic reaction is illustrated from researcher's literature and also from catalyst manufacturer.Mathematical model for such water gas shift reaction is beneficial for study of Concentration profile & Temperature profile. Thus we could get smooth curve for concentration profile by doing modeling and simulation of such catalytic reaction. The main aim of modeling and simulation of any reaction are to provide or compare appropriate kinetics for particular reaction and also sometimes it used to comparison among different catalysts.

Key Words: Water- gas Shift Reactor, Reversible reaction, catalysts, Thermodynamic equilibrium, Ideal plug flow reactor, fixed bed reactor.

1. INTRODUCTION

Today Hydrogen is most important energy source and also reactant for Synthesis gas phase reaction. This way we are interesting to enhance hydrogen or energy sources by different kinds of reactions. For examples we can enhance hydrogen in syntheses gas comes from reformer. Synthesis gas from reformer contain carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), nitrogen (N_2), methane (CH_4) and some inert at dry basis. So we can improve yield of hydrogen by shift conversion of CO to CO_2 by reaction with Steam. This reaction is called Water Gas Shift reaction. This type of conversion is used mostly all hydrogen/ammonia plant.The WGS reaction is reversible and exothermic (ΔH^o = –41.2 kJ/mol). Due to its moderate exothermic, the WGS reaction is thermodynamically unfavourable at elevated temperatures.

2.MODELING OF WGS REACTION
2.1 Thermodynamics of WGS Reaction
Water Gas Shift (WGS) is reversible reaction. So both the forward and reverse reaction is with thermodynamic equilibrium.The true dimensionless equilibrium constant can predict from Gibb's free energy as denoted by the following reaction.

$$R*T*lnK = -\Delta G \qquad (1)$$

Where,
R   = Ideal Gas Constant
T   = Temperature of Reaction, K
K   = Equilibrium Constant
ΔG = Change in Gibb's free Energy, cal/mol

2.2 Design equation for Reactor

All fixed Bed catalytic reactor assumed to behave like ideal plug flow reactor. Equation used for the design or sizing of fixed bed reactor is

$$F_{Ao}(dX/dW) = -r_A \qquad (2)$$

Where,
W = Mass of catalyst
F_{Ao}= Molar flow rate of limiting reactant in feed
X = Fractional conversion of limiting reactant A
$-r_A$= Overall rate of reaction

The differential form of the design equation must be used when analyzing reactors that have a pressure drop along the length of the reactor. Integrating with the limits W=0 at X=0 gives,

$$W = F_{Ao}\int(dX/-r_A)$$

This equation can be used to determine the catalyst weight W necessary to achieve a conversion X when the total pressure remains constant.

2.3 The rate law

Various manufacturers suggest rate equations for their catalysts. This rate equation is based on experiment results, mechanism and catalyst property. We will go to use Equation (1) to define rate law. [12]

$$(-r_{CO}) = \Psi k(y_{CO}\, y_{H2O} - y_{CO2}\, y_{H2}/K)/(\rho b) \qquad (3)$$

This Micro-kinetic model is given by various catalyst manufacturers and based on mole fraction of species. It consider the following factors like Specific rate constant, Activity factor, Equilibrium constant and catalyst bulk density. Here complete rate expression is based on mole fraction so unit of specific rate constant is similar to zero order reaction i.e. mole/m^3 hr.

Where,

k = Rate Constant, lb mole/cu ft, hr
  = exp(15.95 – 8820/T) for iron catalyst
  =exp(12.88 – 3340/T) for Copper-zinc catalyst

K = Equilibrium Constant
  = exp(– 4.72+8640/T) for $760 \leq T \leq 1060$
  = exp(– 4.33+8240/T) for $1060 \leq T \leq 1360$

P = pressure
$(– r_{CO})$ = rate of CO converted
T = Temperature, ^{o}R
y_i = mole fraction of component indicated
ρ_b = Catalyst Bulk density
Ψ = activity factor

For Iron catalyst
Ψ = 0.816 + 0.184P for $P \leq 11.8$
  = 1.53 + 0.123P for $11.8 < P \leq 20.0$
  = 4.0 for $P > 20.0$

For Copper-zinc catalyst
Ψ = 0.86 + 0.14P for $P \leq 24.8$
  = 4.33 for $P > 24.8$

2.4 Material Balance for WGS Reaction.

The concentration for Species A is the number of moles of A per unit volume at given time. Concentration of species A,
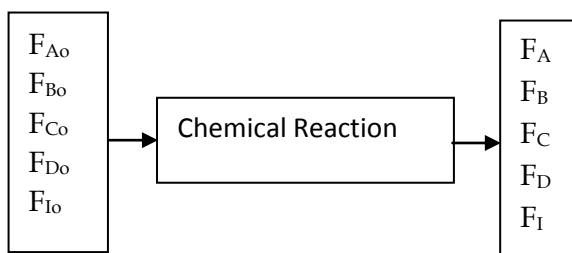
$C_A = F_A/v$

Where,
C_A = Concentration of species A, moles/liter
F_A = molar flow rate of species A, moles/time
v = volumetric flow rate, liters/time

Entering   Leaving

We now can write the concentrations of A, B, C, and D for the general in terms of the entering molar flow rate (F_{Ao}, F_{Bo}, F_{Co} , F_{Do}), the conversion X, and the volumetric flow rate, v.

$C_A = (F_A/v) = (F_{Ao}/v)(1 – X)$
$C_B = (F_B/v) = [F_{Bo} – (b/a) F_{Ao} X]/v$
$C_C = (F_C/v) = [F_{Co} – (c/a) F_{Ao} X]/v$
$C_D = (F_D/v) = [F_{Do} – (d/a) F_{Ao} X]/v$
Now,
Θ_B = Ration of Initial mole of B and A
= $(F_{Bo}/F_{Ao}) = (C_{Bo}/C_{Ao}) = (y_{Bo}/y_{Ao})$

Similarly we can write for Θ_C, Θ_D & Θ_B.
Now, Equation for concentration C_A, C_B , C_C & C_D becomes,

$C_A = C_{Ao} (1 – X)$

$C_B = C_{Bo}[\Theta_B – (b/a)X]$

$C_C = C_{Co}[\Theta_C + (c/a)X]$

$C_D = C_{Do}[\Theta_D + (d/a)X]$ (4)

Where,
T_o = Initial Temperature of Reactant
T = Final Temperature of Product

The above equation is used for relate Concentration as function of Conversion and total mole of feed is remain constant is F_T.

2.5 Combination of all three steps

We have Design equation for packed bed Reactor is

$(dX/dW) = \Psi k(y_{CO} y_{H2O} – y_{CO2} y_{H2}/K)/(F_{COo}\rho_b)$

Now we can put mole fraction of all the compound as a function of Conversion

$y_{CO} = F_{COo} (1 – X)/F_T$

$y_{H2O} = F_{COo} (\Theta_{H2O} – X)/F_T$

$y_{CO2} = F_{COo} (\Theta_{CO2} + X)/F_T$

$y_{H2} = F_{COo} (\Theta_{H2} + X)/F_T$

$(dX/dW)=\Psi k y_{COo}^2[(1 – X)(\Theta_B – X) – (\Theta_C + X)(\Theta_D + X)/K]/(F_{COo}\rho_b)$ (5)

This is design model for Catalytic plug flow for Isothermal case. This ODE can solve from polymath, Scilab ormatleb.

Where,
k = Rate Constant
  = exp(15.95 – 8820/T) for iron catalyst

=exp(12.88 – 3340/T) for Copper-zinc catalyst

K = Equilibrium Constant

= exp(– 4.72+8640/T) for $760 \leq T \leq 1060$

= exp(– 4.33+8240/T) for $1060 \leq T \leq 1360$

P = pressure, atm

$(- r_{CO})$ = rate, kmoles CO converted/kg-catalyst hr

T = Temperature, ^{o}R

y_{COo}= Initial mole fraction of CO

ρb = Catalyst Bulk density, kg/cu m

Ψ = activity factor

For Iron catalyst

Ψ = 0.816 + 0.184P for $P \leq 11.8$

= 1.53 + 0.123P for $11.8 < P \leq 20.0$

= 4.0 for P > 20.0

For Copper-zinc catalyst

Ψ = 0.86 + 0.14P for $P \leq 24.8$

= 4.33 for P > 24.8

3. RESULT AND DISCUSSION

We are first take complete CO conversion based on Copper catalyst and put all the values in equation (5) and solve ODE. Only specific rate constant and catalyst bulk density is different for both catalysts.

Catalyst: Copper-Zinc catalyst

Temperature T = 254 ^{o}C = 527 K = 948.89 ^{o}R

Pressure P = 24 atm

Total Feed Rate, F_T =10000 kmol/hr

F_{CO0} = 960 kmol/hr

F_{H2O0} = 3350 kmol/hr

F_{CO20} = 550 kmol/hr

F_{H20} = 4600 kmol/hr

Now,

Ratio of initial moles of H_2O to CO, Θ_{H2O} = 3.49

Ratio of initial moles of CO_2 to CO, Θ_{CO2} = 0.57

Ratio of initial moles of H_2 to CO, Θ_{H2} = 4.79

Equilibrium constant K at 254 ^{o}C = 81

And value of specific reaction rate constant, k = 181085.61

Ψ = 4.33 at pressure P=24 atm for copper catalyst

Bulk density of Catalyst = 1442 kg/m^3 for copper catalyst

Initial Mole fraction of CO, y_{COo}= 960/10000 = 0.096

Substitute all the values in above equation (5) and write this equation in polymath solver as shown in table – 1.

Conversion X (%)	Weight of Catalyst, W kg	Space Velocity W/FAo, Kg Catalyst* hr/kmol CO
0	0	0
2.882646	600.777	0.625809
11.23314	2481.979	2.585395
25.34637	6250	6.510417
30.09736	7730.219	8.052311
41.33834	11807.83	12.29982
51.67882	16539.62	17.22877
60.74803	21875	22.78646
70.05957	29259.82	30.47898
80.38521	41964.34	43.71285
90.33262	68750	71.61458
95.0871	125000	130.2083

Table – 1 Output results of Space Velocity for given case

3.2 Concentration and Temperature profile

We have two dimensional mathematical model is

$$D_L[d^2C_A/dz^2] – [d(C_Au_z)/dz]+\rho_b r_v = 0$$

Where,

C_A= Concentration of species A (CO)

z = Length of reactor

ρ_b= Bulk density of Catalyst bed

r_w= Rate of reaction of CO converted

u_z= Average velocity in the bed

l = fractional length

D_L= Axial Dispersion

Rate of Reaction is again we can use equation (5)

$$(- r_{CO})= \Psi k y_{COo}^2[(1 – X)(\Theta_B – X) – (\Theta_C + X)(\Theta_D + X)/K]/F_{COo}(\rho b)$$

Initial concentration of CO is found by the equation C = yP/RT, where R is universal gas constant. We can relate temperature of bed with conversion from energy balance so

$$T = T_o + X[\Delta Hrx]$$

Where,

T = Temperature of Bed, ^{o}C

T_o = Initial temperature, ^{o}C

X = Conversion

= Heat of reaction, KJ/mol

Weight of Catalyst(W) Vs Conversion(X)
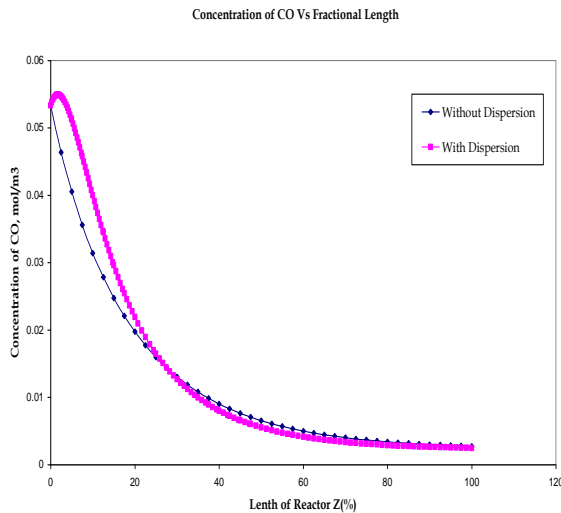
Concentration of CO Vs Fractional Length
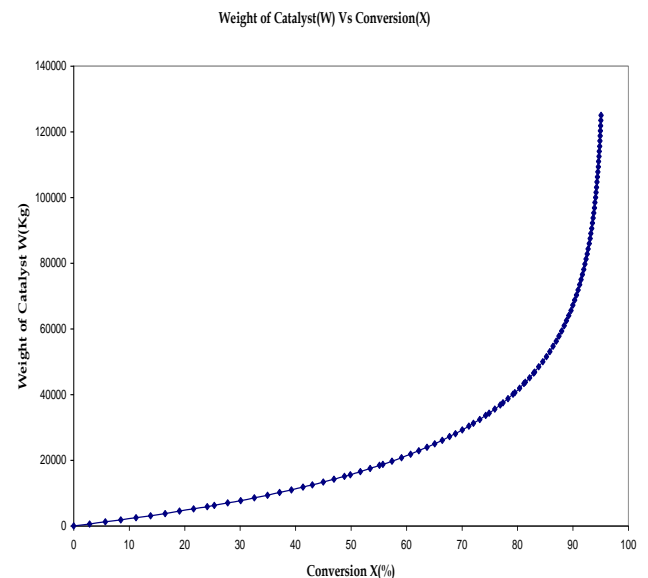
Figure – 1 Space velocity & Concentration Profile

4. CONCLUSION

Water-gas shift reaction is important fuel processing reaction for enhance hydrogen in reformed gas mixture. We can find the space velocity, concentration & temperature profile though out the reactor of the WGS reaction. We can also compare the performance of Catalyst if we have activity coefficient of diff catalyst as show in figure
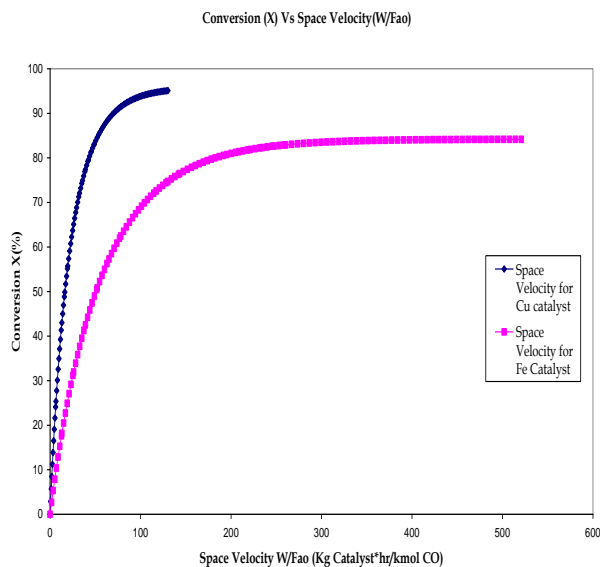
Conversion (X) Vs Space Velocity(W/Fao)

Figure – 6.1 Space velocity comparisons between Iron Oxide and copper-zinc catalyst

5. FUTURE SCOPE

We can develop generalize model for all type of operation: Isothermal as well as adiabatic.This study are developed modeling and simulation based on certain assumption by countering this assumption one's can develop model more complex. Comparison of different catalyst is possible by using modeling and simulation and we can find out best catalyst from that study.Cost estimation of reactor is much

easy by developing appropriate model for particular reaction and condition.Further work is possible on Study of mechanism of chemical reaction and development of Rate low.

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